

Prepolymers with alkoxy silane end groups

The invention relates to alkoxy silane-terminated prepolymers and to compositions comprising prepolymers.

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Prepolymer systems which possess reactive alkoxy silyl groups have been known for a long time and are widely used for producing elastic sealants and adhesives in the industrial and construction sectors. In the presence of atmospheric humidity and appropriate catalysts these alkoxy silane-terminated prepolymers are capable even at room temperature of undergoing condensation with one another, with the elimination of the alkoxy groups and the formation of an Si-O-Si bond. Consequently these prepolymers can be used, *inter alia*, as one-component systems, which possess the advantage of ease of handling, since there is no need to measure out and mix in a second component.

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A further advantage of alkoxy silane-terminated prepolymers lies in the fact that curing is not accompanied by release either of acids or of oximes or amines. Moreover, in contrast to isocyanate-based adhesives or sealants, no CO₂ is formed either, which as a gaseous component can lead to bubbles forming. In contrast to isocyanate-based systems, alkoxy silane-terminated prepolymer mixtures are also toxicologically unobjectionable in each case. Depending on the amount of alkoxy silane groups and their structure, the curing of this type of prepolymer is accompanied by the formation principally of long-chain polymers (thermoplastics), relatively wide-meshed three-dimensional networks (elastomers) or else highly crosslinked systems (thermosets).

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Alkoxy silane-terminated prepolymers may be composed of different units. These prepolymers typically possess an organic backbone; in other words they are composed, for

example of polyurethanes, polyethers, polyesters, polyacrylates, polyvinyl esters, ethylene-olefin copolymers, styrene-butadiene copolymers or polyolefins, described inter alia in EP 0 372 561, 5 EP 0 269 819, WO 00/37533, US 6,207,766, and US 3,971,751. In addition, however, systems whose backbone is composed entirely or at least partly of organosiloxanes are also widespread, and are described inter alia in WO 96/34030 and US 5,254,657.

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One particularly advantageous preparation process for alkoxy silane-terminated prepolymers starts from polyols, such as from polyether or polyester polyols, which in a first reaction step are reacted with an 15 excess of a di- or polyisocyanate. Subsequently the resultant isocyanate-terminated prepolymers are reacted with a γ -aminopropyl-functional alkoxy silane to give the desired alkoxy silane-terminated prepolymer. Systems of this kind are described for example in EP 1 256 595, 20 EP 0 569 360 or EP 0 082 528 or DE 198 49 817.

Such systems still have a number of disadvantages, however. One disadvantage is their no more than moderate reactivity with respect to moisture, either in 25 the form of atmospheric humidity or in the form of existing or added water. In order to achieve a sufficient cure rate at room temperature it is therefore vital to add a catalyst. The principal reason why this presents problems is that the organotin 30 compounds commonly employed as catalysts are toxicologically objectionable. Moreover, the tin catalysts often also contain traces of highly toxic tributyltin derivatives.

35 A particular problem is the relatively low reactivity of the alkoxy silane-terminated prepolymers if the terminations used are not methoxysilyls but rather the even less reactive ethoxysilyls. Ethoxysilyl-terminated

prepolymers specifically, however, would be particularly advantageous in many cases since their curing is accompanied by the release only of ethanol as a cleavage product.

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In order to circumvent this problem, attempts have already been made to look for tin-free catalysts. Consideration might be given here, in particular, to titanium catalysts, such as titanium tetraisopropoxide 10 or bis(acetylacetonato)diisobutyl titanate (described *inter alia* in EP 0 885 933). These titanium catalysts, though, possess the disadvantage that they cannot be used together with numerous nitrogen compounds, since the latter act here as catalyst poisons. The use of 15 nitrogen compounds, as adhesion promoters for example, would nevertheless be desirable in many cases. Moreover, nitrogen compounds, aminosilanes for example, serve in many cases as reactants in the preparation of the silane-terminated prepolymers.

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Accordingly, alkoxy silane-terminated prepolymer systems of the kind described, in DE 101 42 050, DE 101 39 132, DE 21 55 259, DE 21 55 258, DE 1 905 100 and DE 1 812 564 may represent a great advantage. A feature 25 of these prepolymers is that they contain alkoxy silyl groups separated only by a methyl spacer from an electronegative heteroatom having at least one free electron pair, i.e., from an oxygen, nitrogen or sulfur atom. As a result, these prepolymers possess extremely 30 high reactivity with respect to (atmospheric) humidity, and accordingly can be processed to prepolymer blends which can manage even with little catalyst or even without catalysts which contain titanium, tin or other (heavy) metals, and yet cure at room temperature with 35 sufficiently short tack-free times and at a sufficiently high rate.

All alkoxy silane-terminated prepolymers of the prior

art, however, have the disadvantage that they cure only to materials having a moderate tensile strength and/or breaking elongation. The sole exception here are systems with a high level of urea units in the 5 prepolymer, as described in DE 21 55 259 or DE 21 55 258. However, this high level of urea units means that even in the uncrosslinked state these prepolymers are solid and can be handled only in highly diluted solutions with a solids content << 50%. For the 10 majority of applications prepolymer solutions of this kind are completely unsuitable.

Silane-crosslinking blends which cure to materials with high tensile strength and breaking elongation are 15 sought in particular for adhesive applications. One approach to improving the tensile strength of alkoxy silane-crosslinking adhesives may be represented by the use of optimized filler mixtures incorporated into the alkoxy silane-terminated polymer. One such 20 process is described in EP 1 256 595. There, a particular variety of carbon black is mixed, along with finely divided, coated calcium carbonate, into an alkoxy silane-terminated prepolymer. Although this 25 system did allow outstanding tensile strengths to be achieved, of 4.5 - 5.9 MPa, the breaking elongations that were achievable were very mediocre at 250% - 300%. Moreover, only black adhesives can be produced using 30 carbon black-filled materials of this kind. Other colors, although often desired, are not possible. Furthermore, it may be desirable to omit fillers 35 entirely, if, for example, transparent materials are required for optical reasons. A further disadvantage of the materials described in EP 1 256 595 is, additionally, the above-described moderate reactivity with respect to moisture, particularly with respect to atmospheric humidity.

There is therefore still a requirement for not only

blends of silane-terminated prepolymers but also the silane-terminated prepolymers themselves to be improved with respect to the prior art. The improved prepolymers are not only to be distinguished by a high reactivity with respect to atmospheric humidity but are also to have an improved tensile strength and also a considerably improved breaking elongation.

The invention provides prepolymers (A) having end groups of the general formula [1]



where

15 A is a divalent linking group selected from -O-,
-S-, -(R³)N-, -O-CO-N(R³)-, -N(R³)-CO-O-,
-NH-CO-NH-, -N(R⁴)-CO-NH-, -NH-CO-N(R⁴)-, and
-N(R⁴)-CO-N(R⁴)-,
20 R¹ is an optionally halogen-substituted alkyl,
cycloalkyl, alkenyl or aryl radical having 1-10
carbon atoms,
R² is an alkyl radical having 1-6 carbon atoms or an
ω-oxaalkyl-alkyl radical having in all 2-10 carbon
atoms,
25 R³ is hydrogen, an optionally halogen-substituted
cyclic, linear or branched C₁ to C₁₈ alkyl radical
or alkenyl radical or a C₆ to C₁₈ aryl radical,
R⁴ is an optionally halogen-substituted cyclic,
linear or branched C₁ to C₁₈ alkyl radical or
30 alkenyl radical or a C₆ to C₁₈ aryl radical, and
a has the value 0, 1 or 2,
the prepolymers (A) being obtainable by reacting
isocyanate-functional prepolymers (A1) with alkoxy-
silanes (A2) possessing at least one isocyanate-
35 reactive group,
and optionally further components,
with the proviso that the alkoxy silanes (A2) are
employed in excess, so that the ratio of isocyanate-

reactive groups to isocyanate groups is at least 1.2:1.

The prepolymers (A) thus prepared exhibit a high reactivity with respect to atmospheric humidity. After 5 crosslinking, they have, independently of any fillers used, a considerably improved tensile strength and also a considerably improved breaking elongation. Compositions (M) as well which comprise the silane-terminated prepolymers (A) exhibit the improved tensile 10 strength and breaking elongation.

The prepolymers (A) are isocyanate-free. In addition, they are distinguished by the fact that they contain 15 alkoxy silyl groups of the general formula [1] separated only by a methyl spacer from an electronegative heteroatom having at least one free electron pair. As a result, the prepolymers (A) possess an extremely high reactivity toward (atmospheric) humidity, and can therefore be processed to polymer blends (M) which, 20 even with little or even no tin catalyst, preferably with no tin or titanium catalyst, more preferably entirely without heavy metal catalyst, cure at room temperature with sufficiently short tack-free times and at a sufficiently high rate.

25 Preferred radicals R^1 are methyl, ethyl or phenyl groups. The radicals R^2 are preferably methyl or ethyl groups, hydrogen is preferred as radical R^3 , while the radicals R^4 are preferably alkyl radicals having 1-4 30 carbon atoms, cyclohexyl radicals, and phenyl radicals.

Particular preference is given to alkoxy silyl-terminated prepolymers (A) whose crosslinkable 35 alkoxy silyl groups are separated by a methyl spacer from a urethane or urea group, i.e., polymers (A) of the general formula [1] in which A is selected from the groups $-NH-CO-O$ and $-NH-CO-N(R^3)-$.

In the preparation of the prepolymers (A), the alkoxy-silane component (A2) is preferably employed in an excess, so that the ratio of isocyanate-reactive groups to isocyanate groups is 1.4:1 to 4:1, in particular 5 1.5:1 to 2.5:1.

Particularly advantageous properties are possessed in this context by prepolymers (A) which are terminated with alkoxy-silyl groups of the general formula [1] if 10 at least 50%, in particular at least 70%, of these alkoxy-silyl groups are composed of dialkoxy-silyl groups (a = 1). Prepolymers (A) containing exclusively dialkoxy-silyl groups of the general formula [1] are not only particularly preferred but also easy to obtain 15 logistically, since their preparation requires only one type of silane (A4).

The main chains of the alkoxy-silane-terminated polymers (A) may be branched or unbranched, preference being 20 given to main chains which are unbranched or have only low degrees of branching. The average chain lengths can be adapted arbitrarily, in accordance with the particular desired properties both of the uncrosslinked mixture and of the cured material.

25 In the preparation of the prepolymers (A), preferably urethane-group-containing prepolymers are employed as isocyanate-functional prepolymers (A1), as are obtainable by a reaction of polyols (A11) and with di- or 30 polyisocyanates (A12).

As polyol component (A11) for the preparation of the isocyanate-functional prepolymers (A1) it is possible in principle to use all polyols having a preferred 35 average molecular weight Mn of 1000 to 25 000. These may be, for example, hydroxyl-functional polyethers, polyesters, polyacrylates and polymethacrylates, polycarbonates, polystyrenes, polysiloxanes, polyamides,

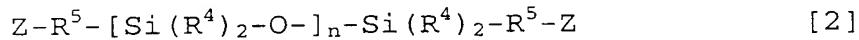
polyvinyl esters, polyvinyl hydroxides or polyolefins such as polyethylene, polybutadiene, ethylene-olefin copolymers or styrene-butadiene copolymers, for example.

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Preference is given to using polyols (A11) having an average molecular weight M_n of 2000 to 25 000, more preferably of 4000 to 20 000. Particularly suitable polyols (A11) are aromatic and/or aliphatic polyester 10 polyols and polyether polyols, of the kind widely described in the literature. The polyethers and/or polyesters that are used as polyols (A11) may be either linear or branched, although preference is given to unbranched, linear polyols. Moreover, polyols (A11) may 15 also possess substituents such as halogen atoms.

As polyols (A11) it is also possible as well to use hydroxyalkyl- or aminoalkyl-terminated polysiloxanes of the general formula [2]

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in which

25 R^5 is a hydrocarbon radical having 1 to 12 carbon atoms, preferably methyl radicals,
30 R^6 is a branched or unbranched hydrocarbon chain having 1-12 carbon atoms, preferably n-propyl,
 n is a number from 1 to 3000, preferably a number from 10 to 1000, and
 Z is an OH or NHR^3 group

and R^3 is as defined for the general formula [1].

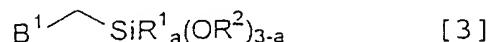
35 It will be appreciated that the use of any desired mixtures of the various types of polyol is also possible. Particular preference, however, is given to using linear polyether polyols as polyols (A11), with polypropylene glycols especially having particularly

high suitability.

As di- or polyisocyanates (A12) for preparing the isocyanate-functional prepolymers (A1) it is possible in principle to use all customary isocyanates, of the kind widely described in the literature. Common diisocyanates (A12) are, for example, diisocyanato-diphenylmethane (MDI), both in the form of crude or technical MDI and in the form of pure 4,4' and/or 2,4' isomers or mixtures thereof, tolylene diisocyanate (TDI) in the form of its various regioisomers, diisocyanatonaphthalene (NDI), isophorone diisocyanate (IPDI), perhydrogenated MDI (H-MDI) or else hexamethylene diisocyanate (HDI). Examples of polyisocyanates (A3) are polymeric MDI (P-MDI), triphenylmethane triisocyanate, or isocyanurate triisocyanates or biuret triisocyanates. All di- and/or polyisocyanates (A12) can be used individually or else in mixtures. It is preferred, however, to use exclusively diisocyanates. If the UV stability of the prepolymers (A) or of the cured materials produced from these prepolymers is significant because of the particular application, it is preferred to use aliphatic isocyanates as component (A12).

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As alkoxy silanes (A2) for preparing the prepolymers (A) it is possible in principle to use all alkoxy silanes which possess an isocyanate-reactive group. The alkoxy silanes serve to incorporate the alkoxy silyl terminations into the prepolymers (A). As alkoxy silanes (A2) it is preferred to use compounds selected from silanes of the general formulae [3]



where

35 B^1 is an OH, SH or NH₂ group or a group HR³N and R¹, R², R³ and a are as defined for the general

formula [1].

5 B^1 is the isocyanate-reactive group. The group B^1 is preferably the HR^3N group. The prepolymers (A) then have a high curing rate.

10 It is possible in this context to use individual silanes (A2) and also mixtures of different silanes (A2). The silanes in question can be prepared by a reaction of chloromethyltrialkoxysilane, chloromethyl-dialkoxyethylsilane or chloroalkoxydimethylsilane with an amine of the formula NH_2R^3 , in other words from very simple and inexpensive reactants, in only one reaction step, without problems.

15 The prepolymers (A) are prepared by simply combining the components described, with the possible addition, if desired, of a catalyst and/or with the possibility, if desired of working at elevated temperature.

20 In one preferred method a polyol component (A11) is initially reacted with a di- and/or polyisocyanate component (A12) and also, optionally, further components. On account of the relatively high 25 exothermicity of these reactions it may be advantageous to add the individual components in succession in order to allow better control of the quantity of heat given off. Thereafter the resultant isocyanate-terminated prepolymer (A1) is reacted with the alkoxysilane component (A2) and also, if desired, with further 30 components. As described, the alkoxysilane component (A2) is used in excess. Preferably in this case component (A2) is added with vigorous stirring in one go or at least very rapidly, i.e., within a few 35 minutes, so that the period of time during which component (A2) is present in deficit amount is limited to a few minutes. An alternative possibility is to introduce component (A2) in excess, initially, and to

add components (A1). Also imaginable in principle is a continuous preparation of prepolymer, in a tube reactor, for example. Separate purification or other workup of the prepolymer (A) is not generally required.

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In one preferred embodiment of the invention the concentration ratios during the prepolymer preparation and the reaction conditions are selected such that at least 70%, preferably at least 80%, in particular at least 90% of the chain ends of the prepolymers (A) are terminated with alkoxy silyl groups of the general formula [1].

The reactions between isocyanate groups and isocyanate-reactive groups which occur during the preparation of the prepolymers (A) can if desired be accelerated by means of a catalyst. It is preferred in this case to use the same catalysts listed below as curing catalysts (C). It may even be possible for the preparation of the prepolymers (A) to be catalyzed by the same catalysts which later also serve as curing catalysts (C) when curing the finished prepolymer blends. This has the advantage that the curing catalyst (C) is already present in the prepolymer (A) and need no longer be added separately during the compounding of the finished prepolymer blend. It will be appreciated that in lieu of one catalyst it is also possible to employ combinations of two or more catalysts.

In order to achieve rapid curing of the blends of the prepolymers (A) at room temperature it is possible if desired to add a curing catalyst (C). As already mentioned, suitable catalysts here include, among others, the organotin compounds typically used for this purpose, such as dibutyltin dilaurate, dioctyltin dilaurate, dibutyltin diacetylacetone, dibutyltin diacetate or dibutyltin dioctoate, etc. In addition it is also possible to use titanates, e.g., titanium(IV)

isopropoxide, iron(III) compounds, e.g., iron(III) acetylacetone, or else amines, e.g., triethylamine, tributylamine, 1,4-diazabicyclo[2.2.2]octane, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene, N,N-bis(N,N-dimethyl-2-aminoethyl)-methylamine, N,N-dimethylcyclohexylamine, N,N-dimethyl-phenylamine, N-ethylmorpholine, etc. Organic or inorganic Brønsted acids as well, such as acetic acid, trifluoroacetic acid or benzoyl chloride, hydrochloric acid, phosphoric acid and its mono- and/or diesters, such as butyl phosphate, (iso)propyl phosphate, dibutyl phosphate, etc., are suitable as catalysts (C). In addition, however, it is also possible here to use numerous further organic and inorganic heavy metal compounds and also organic and inorganic Lewis acids or Lewis bases. Moreover, the crosslinking rate may also be increased further, or matched precisely to the particular requirement, by means of combining different catalysts or combining catalysts with different cocatalysts. Distinct preference is given here to blends which comprise prepolymers (A) having highly reactive alkoxy silyl groups of the general formula [1], and hence do not require heavy metal catalysts (C), in order to achieve cure times which are sufficiently short even at room temperature.

The use of prepolymers (A) having silane termini of the general formula [1] has the particular advantage, moreover, that it allows the preparation even of compositions (M) which contain exclusively ethoxysilyl groups, i.e., silyl groups of the general formula [1] with $R^2 = \text{ethyl}$. The moisture reactivity of these compositions (M) is such that even without tin catalysts they cure at a sufficiently high rate, despite the fact that ethoxysilyl groups generally are less reactive than the corresponding methoxysilyl groups. Thus even with ethoxysilane-terminated polymers (A) tin-free systems are possible. Polymer blends (M)

of this kind, containing exclusively ethoxysilane-terminated polymers (A), possess the advantage that on curing they release only ethanol as a cleavage product. They represent a preferred embodiment of this 5 invention.

The prepolymers (A) are preferably employed in blends which besides the silanes (A2) added in excess in the prepolymer synthesis additionally comprise low 10 molecular weight alkoxy silanes (D). These alkoxy silanes (D) may take on a number of functions. For example, they may serve as water scavengers - that is, they are intended to scavenge any traces of moisture that may be present, and so to increase the storage stability of 15 the corresponding silane-crosslinking compositions (M). It will be appreciated that their reactivity toward traces of moisture must be at least comparable with that of the prepolymer (A). Suitability as water scavengers is therefore possessed in particular by 20 highly reactive alkoxy silanes (D) of the general formula [4]



where

25 B^2 is a group $\text{R}^3\text{O}-\text{CO}-\text{NH}$, $\text{R}^3\text{R}^3\text{N}-\text{CO}-\text{NH}$, OR^3 , SR^3 , NH_2 , NHR^3 or $\text{N}(\text{R}^3)_2$ and
 R^1 , R^2 , R^3 and a are as defined for the general formula [1]. A particularly preferred water scavenger is the carbamatosilane in which B^2 is a group $\text{R}^3\text{O}-\text{CO}-\text{NH}$.

30 The low molecular weight alkoxy silanes (D) may, furthermore, also serve as crosslinkers and/or reactive diluents. Suitability for this purpose is possessed in principle by all silanes which possess reactive alkoxy silyl groups via which they can be incorporated, 35 during the curing of the polymer blend, into the three-dimensional network that forms. The alkoxy silanes (D) may in this case contribute to an increase in the

network density and hence to an improvement in the mechanical properties, such as the tensile strength, of the cured material. Moreover, they may also lower the viscosity of the prepolymer blends in question.

5 Examples of suitable alkoxy silanes (D) in this function include alkoxy methyltrialkoxy silanes and alkoxy methyl-dialkoxy alkyl silanes. Preferred alkoxy groups are methoxy and ethoxy groups. Furthermore, the inexpensive alkyltrimethoxysilanes, such as methyltrimethoxysilane

10 and also vinyl- or phenyltrimethoxysilane, and their partial hydrolysates, may also be suitable.

The low molecular weight alkoxy silanes (D) may additionally serve as adhesion promoters. Here it is

15 possible in particular to use alkoxy silanes which possess amino functions or epoxy functions. Examples that may be mentioned include γ -aminopropyltrialkoxy silanes, γ -[N-aminoethylamino]propyltrialkoxy silanes, γ -glycidyloxypropyltrialkoxy silanes, and all

20 silanes corresponding to the formula [4] in which B^2 is a nitrogen-containing group.

Finally, the low molecular weight alkoxy silanes (D) may even serve as curing catalysts or cocatalysts.

25 Suitability for this purpose is possessed in particular by all basic amino silanes, such as all aminopropyl silanes, N-aminoethylaminopropyl silanes, and also all silanes corresponding to the formula [4] with the proviso that B^2 is an NH_2 group or a group NHR^4 or

30 $N(R^4)_2$.

The alkoxy silanes (D) can be added to the prepolymers (A) at any desired point in time. Where they do not possess NCO-reactive groups, they can even be added

35 during the synthesis of the prepolymers (A). In this context it is possible, based on 100 parts by weight of prepolymer (A), to add up to 100 parts by weight, preferably 1 to 40 parts by weight, of a low molecular

weight alkoxy silane (D).

Furthermore, fillers (E) are typically added to blends of the alkoxy silane-terminated prepolymers (A). These 5 fillers (E) lead to a considerable improvement in the properties of the resultant blends (M). The tensile strength in particular, and also the breaking elongation, can be raised considerably through the use of appropriate fillers.

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Appropriate fillers (E) include all materials of the kind widely described in the prior art. Examples of fillers are nonreinforcing fillers, i.e. fillers having a BET surface area of up to 50 m²/g, such as quartz, 15 diatomaceous earth, calcium silicate, zirconium silicate, zeolites, calcium carbonate, metal oxide powders, such as aluminum, titanium, iron or zinc oxides and/or their mixed oxides, barium sulfate, calcium carbonate, gypsum, silicon nitride, silicon 20 carbide, boron nitride, powdered glass and powdered polymers; reinforcing fillers, i.e. fillers having a BET surface area of at least 50 m²/g, such as pyrogenic (fumed) silica, precipitated silica, carbon black, such as furnace black and acetylene black, and 25 silicon/aluminum mixed oxides of high BET surface area; and fibrous fillers, such as asbestos and also polymeric fibers. Said fillers may have been hydrophobicized, by treatment for example with organosilanes or organosiloxanes or by etherification 30 of hydroxyl groups to alkoxy groups. It is possible to use one kind of filler (E); it is also possible to use a mixture of at least two fillers (E).

The fillers (E) are used preferably in a concentration 35 of 0-90% by weight, based on the finished blend, with concentrations of 30-70% by weight being particularly preferred. In one preferred application use is made of filler combinations (E) which in addition to calcium

carbonate also include pyrogenic silica and/or carbon black.

5 Compositions (M) which contain no fillers (E) are also preferred. Thus the prepolymers (A) after curing already possess a relatively high breaking elongation, and so allow even unfilled compositions (M). Advantages of unfilled compositions (M) are significantly lower viscosity and also transparency.

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The compositions (M) may additionally also comprise small amounts of an organic solvent (F). The purpose of this solvent is to lower the viscosity of the uncrosslinked compositions. Suitable solvents (F) 15 include in principle all solvents and solvent mixtures. Solvents (F) used preferably are compounds which possess a dipole moment. Particularly preferred solvents possess a heteroatom having free electron pairs which are able to enter into hydrogen bonds. 20 Preferred examples of such solvents are ethers such as tert-butyl methyl ether, esters, such as ethyl acetate or butyl acetate, and alcohols, such as methanol, ethanol and the various regioisomers of propanol and butanol. The solvents (F) are used preferably in a 25 concentration of 0-20% by volume, based on the finished compositions (M) including all fillers (E), particular preference being given to solvent concentrations of 0-5% by volume.

30 Further components which may be present in the compositions (M) include conventional auxiliaries, such as reactive diluents and/or water scavengers other than components (D), and also adhesion promoters, plasticizers, thixotropic agents, fungicides, flame 35 retardants, pigments, etc. Additionally, light stabilizers, antioxidants, free-radical scavengers and further stabilizers may be added to the compositions (M). To produce the particular desired profiles of

properties, both of the uncrosslinked compositions (M) and also of the cured materials (M), additions of this kind are generally indispensable.

5 Countless different applications exist for the compositions (M) in the areas of adhesives, sealants, and joint-sealing compounds, in surface coatings, and also in the production of moldings. On account of their improved tensile strength the compositions (M) are
10 particularly suitable for adhesive applications. The use of the prepolymers (A) in adhesives is therefore preferred. They are suitable for countless different substrates, such as mineral substrates, metals, plastics, glass, ceramics, etc.

15 The compositions (M) can be employed as they are or else in the form of solutions or dispersions.

20 All above symbols in the above formulae have their definitions in each case independently of one another. In all formulae the silicon atom is tetravalent.

25 Unless indicated otherwise, all amounts and percentages are by weight, all pressures are 0.10 MPa (abs.) and all temperatures are 20°C.

30 The measure indicated in each case for the reactivities of the compositions (M) or for the reactivities of the noninventive polymer blends in the comparative examples are the skinning times. By skinning times are meant the time period which elapses following application of the composition (M) in air until the polymer surface has cured to the extent that on contact of said surface with a pencil the composition does not adhere to the
35 pencil and there is no stringing.

Example 1:**Preparation of N-cyclohexylaminomethyldimethoxysilane:**

1486.5 g (15 mol) of cyclohexylamine and 600 g of cyclohexane as solvent are introduced in their entirety
5 into a 4-liter 4-neck flask and this initial charge is subsequently rendered inert using nitrogen. It is heated to a temperature of 85°C, 773.4 g (5 mol) of chloromethylmethyldimethoxysilane are added dropwise over 2 h (temperature < 95°C), and the mixture is
10 stirred at 95°C for 2 hours more. Following the addition of approximately 300 g of the silane there is increasing precipitation of cyclohexylamine hydrochloride in salt form, but the suspension remains readily stirrable until the end of metering. The
15 suspension is left to stand overnight and then approximately 300 ml of cyclohexane added. Under a partial vacuum the excess amine and the cyclohexane solvent are removed by distillation at 60 - 70°C. The residue is cooled and treated with a further 300 ml of
20 cyclohexane in order to precipitate the hydrochloride completely. The suspension is filtered and the solvent is again removed under partial vacuum at 60 - 70°C. The residue is purified by distillation (106 - 108°C at 15 mbar). A yield of 761 g, i.e. 70% of theory, is
25 achieved, with a product purity of approximately 99.5%.

Example 2:**Preparation of methoxymethyltrimethoxysilane (MeO-TMO):**

315 ml of methanol are admixed with gentle stirring
30 with 68 g (1.26 mol) of sodium methoxide. After the sodium methoxide has fully dissolved at 65°C, 205 g (1.2 mol) of chloromethyltrimethoxysilane are added dropwise over the course of 2 h at a temperature of 45 - 50°C. In the course of the slightly exothermic
35 neutralization NaCl is precipitated. This is followed by stirring with slow cooling to 25°C for 1 hour. NaCl is filtered off on a frit of porosity 3 and rinsed with a little methanol.

Under partial vacuum the methanol solvent is removed at 60°C. The residue is purified by distillation (78 - 93°C at 90 mbar). A yield of 140 g, i.e. 70% of theory 5 is achieved.

Example 3:

Preparation of methyl trimethoxysilylmethylcarbamate (C-TMO):

10 61.3 g (7.56 mol) of extra finely ground potassium isocyanate are weighed out into a 1-liter 4-neck flask. Subsequently 404 g (0.51 l, 12.6 mol) of methanol, 184.0 g (0.196 l) of dimethylformamide and 100.7 g (0.59 mol) of chloromethyltrimethoxysilane are 15 introduced. The reaction mixture is heated to boiling, with stirring, and is held under reflux for a total of 10 h, the boiling temperature rising from 100°C to 128°C and then remaining stable. After the mixture has been cooled to room temperature the potassium chloride 20 formed is separated off on a suction filter and the filter cake is washed with 1.1 l of methanol. The methanol and dimethylformamide solvents are removed on a rotary evaporator. The remaining amounts of potassium chloride are separated off. The crude solution is 25 purified by distillation (overhead temperature 79 - 85°C at 3 mbar). In total it was possible to obtain 60.4 g (53% of theory [114 g]) of C-TMO.

Example 4:

30 **Preparation of a prepolymer (A):**

A 250-ml reaction vessel with stirring, cooling and heating means is charged with 152 g (16 mmol) of a polypropylene glycol having an average molecular weight of 9500 g/mol (Acclaim® 12200 from Bayer) and this 35 initial charge is dewatered under reduced pressure at 80°C for 30 minutes. The heating is then removed and, under nitrogen, 7.1 g (32 mmol) of isophorone-diisocyanate and 80 mg of dibutyltin dilaurate

(corresponding to a tin content of 100 ppm) are added. This mixture is then stirred at 80°C for 60 minutes. The NCO-terminated polyurethane prepolymer obtained is then cooled to 75°C and admixed with 13.9 g (64 mmol, 5 corresponds to an excess of 100%) of *N*-cyclohexylamino-methyldimethoxymethylsilane, and the mixture is stirred at 80°C for 60 minutes. In the resulting prepolymer mixture it is no longer possible to detect isocyanate groups by IR spectroscopy. A slightly turbid prepolymer 10 is obtained which at 20°C with a viscosity of 77 Pas can be poured and further-processed without problems.

Preparation of prepolymer blends (M):

General instruction (The specific amounts for the 15 individual components can be taken from Table 1. In the absence of certain components, the respective incorporation steps are omitted.):

The prepolymer (A) described above is admixed with 20 carbamatomethyltrimethoxysilane (C-TMO - prepared according to Example 3) and the components are mixed in a Speedmixer (DAC 150 FV from Hausschild) at 27 000 rpm for 15 seconds. Then chalk (BLR 3 from Omya), HDK V 15 (Wacker Chemie GmbH, Germany) and methoxymethyl-25 trimethoxysilane (MeO-TMO - prepared according to Example 2) are added and mixing is carried out for twice 20 seconds at a speed of 30 000 rpm. Finally aminopropyltrimethoxysilane (A-TMO - Silquest® A1110® from Crompton) is added, followed again by mixing for 30 seconds at a speed of 30 000 rpm.

Table 1:

Batch number	Ex. 4-1	Ex. 4-2	Ex. 4-3
Polymer	96%	65%	60%
Chalk BLR 3	-	30%	30%
HDK V-15	-	-	5%
Silane1	-	1% C-TMO	1% C-TMO
Silane2	2% MeO-TMO	2% MeO-TMO	2% MeO-TMO
Silane3	2% A-TMO	2% A-TMO	2% A-TMO

Comparative Example 1:

This comparative example relates to Example 4. However, no excess of *N*-cyclohexylaminomethyldimethoxymethylsilane is used.

Preparation of a noninventive prepolymer:

A 250-ml reaction vessel with stirring, cooling and heating means is charged with 152 g (16 mmol) of a polypropylene glycol having an average molecular weight of 9500 g/mol (Acclaim[®] 12200 from Bayer) and this initial charge is dewatered under reduced pressure at 80°C for 30 minutes. The heating is then removed and, under nitrogen, 7.1 g (32 mmol) of isophorone-diisocyanate and 80 mg of dibutyltin dilaurate are added. This mixture is then stirred at 80°C for 60 minutes. The NCO-terminated polyurethane prepolymer obtained is then cooled to 75°C and admixed with 6.96 g (32 mmol) of *N*-cyclohexylaminomethyldimethoxymethylsilane, and the mixture is stirred at 80°C for 60 minutes. In the resulting prepolymer mixture it is no longer possible to detect isocyanate groups by IR spectroscopy. A slightly turbid prepolymer is obtained which at 20°C with a viscosity of 278 Pas can be poured and further-processed without problems.

Preparation of noninventive prepolymer blends:

General instruction (The specific amounts for the individual components can be taken from Table 2. In the absence of certain components, the respective incorporation steps are omitted.):

The prepolymer described above is admixed with carbamatomethyltrimethoxysilane (C-TMO - prepared according to Example 3) and the components are mixed in a Speedmixer (DAC 150 FV from Hausschild) at 27 000 rpm for 15 seconds. Then chalk (BLR 3 from Omya), HDK V 15 (Wacker Chemie GmbH, Germany) and methoxymethyl-

trimethoxysilane (MeO-TMO - prepared according to Example 2) are added and mixing is carried out for twice 20 seconds at a speed of 30 000 rpm. Finally aminopropyltrimethoxysilane (A-TMO - Silquest® A1110 from Crompton) is added, followed again by mixing for 20 seconds at a speed of 30 000 rpm.

Table 2:

Batch number	C.Ex. 1-1	C.Ex. 1-2	C.Ex. 1-3
Polymer	96%	65%	60%
Chalk BLR 3	-	30%	30%
HDK V-15	-	-	5%
Silane1	-	1% C-TMO	1% C-TMO
Silane2	2% MeO-TMO	2% MeO-TMO	2% MeO-TMO
Silane3	2% A-TMO	2% A-TMO	2% A-TMO

10 **Example 5:****Properties of the cured prepolymer blends**

This example shows the properties and the preparation of the specimens sample of Example 4 and Comparative Example 1:

15

The finished prepolymer blends are coated out using a doctor blade into a Teflon® mold 2 mm high, the rate of curing through volume being approximately 2 mm in a day. After two-week storage, S1 test specimens are punched out, and their tensile properties measured in accordance with EN ISO 527-2 on the Z010 from Zwick. The properties measured on the respective prepolymer blends are listed in Table 3. The blends of

- Example 4.1, Comparative Example 1.1
- Example 4.2, Comparative Example 1.2
- Example 4.3, Comparative Example 1.3

are in each case identical and differ only in the prepolymer used. In other words, the properties of these compositions can be compared directly with one another in each case.

30

Table 3:

Batch number	Ex. 4-1	Ex. 4-2	Ex. 4-3
Skinning time	> 2 h	> 2 h	55 min
Tensile strength [MPa]	1.02	1.82	2.49
Breaking elongation [%]	561.76	507.99	511.28
Modulus [MPa]	0.24	0.53	0.98
Shore hardness	22	37	41
Batch number	C.Ex. 1-1	C.Ex. 1-2	C.Ex. 1-3
Skinning time	50 min	45 min	35 min
Tensile strength [MPa]	0.71	1.02	1.02
Breaking elongation [%]	515.68	641.75	353.2
Modulus [MPa]	0.09	0.16	0.34
Shore hardness	6	6	19

Example 6:**Preparation of a prepolymer (A):**

5 A 250-ml reaction vessel with stirring, cooling and heating means is charged with 160 g (40 mmol) of a polypropylene glycol having an average molecular weight of 4000 g/mol and this initial charge is dewatered under reduced pressure at 80°C for 30 minutes. The 10 heating is then removed and, under nitrogen, 12.43 g (56 mmol) of isophorone diisocyanate and 80 mg of dibutyltin dilaurate are added. This mixture is stirred at 80°C for 60 minutes. The NCO-terminated polyurethane prepolymer obtained is then cooled to 75°C and admixed 15 with 11.13 g (51.2 mmol - corresponds to an excess of 60%) of *N*-cyclohexylaminomethyldimethoxymethylsilane, and the mixture is stirred at 80°C for 60 minutes. In the resulting prepolymer mixture it is no longer possible to detect isocyanate groups by IR 20 spectroscopy. A slightly turbid prepolymer is obtained which at 20°C with a viscosity of 155 Pas can be poured and further-processed without problems.

Preparation of prepolymer blends (M):

25 General instruction (The specific amounts for the

individual components can be taken from Table 4. In the absence of certain components, the respective incorporation steps are omitted.):

5 The prepolymer described above is admixed with carbamatomethyltrimethoxysilane (C-TMO - prepared according to Example 3) and the components are mixed in a Speedmixer (DAC 150 FV from Hausschild) at 27 000 rpm for 15 seconds. Then chalk (BLR 3 from Omya), HDK V 15
 10 (Wacker Chemie GmbH, Germany) and methoxymethyltrimethoxysilane (MeO-TMO - prepared according to Example 2) are added and mixing is carried out for twice 20 seconds at a speed of 30 000 rpm. Finally aminopropyltrimethoxysilane (A-TMO - Silquest® A1110
 15 from Crompton) is added, followed again by mixing for 20 seconds at a speed of 30 000 rpm.

Table 4:

Batch number	C.Ex. 2-1	C.Ex. 2-2	C.Ex. 2-3
Polymer [%]	96%	65%	60%
Chalk BLR 3 [%]	-	30%	30%
HDK V-15 [%]	-	-	5%
Silane 1 [%]	-	1% C-TMO	1% C-TMO
Silane 2 [%]	2% MeO-TMO	2% MeO-TMO	2% MeO-TMO
Silane 3 [%]	2% A-TMO	2% A-TMO	2% A-TMO

20 **Comparative Example 2:**

This comparative example relates to Example 5. However, no excess of *N*-cyclohexylaminomethyldimethoxymethylsilane is used.

25 **Preparation of a noninventive prepolymer:**

A 250-ml reaction vessel with stirring, cooling and heating means is charged with 160 g (40 mmol) of a polypropylene glycol having an average molecular weight of 4000 g/mol and this initial charge is dewatered
 30 under reduced pressure at 80°C for 30 minutes. The heating is then removed and, under nitrogen, 12.43 g

(56 mmol) of isophoronediisocyanate and 80 mg of dibutyltin dilaurate are added. This mixture is stirred at 80°C for 60 minutes. The NCO-terminated polyurethane prepolymer obtained is then cooled to 75°C and admixed 5 with 6.96 g (32 mmol) of *N*-cyclohexylaminomethyl-dimethoxymethylsilane, and the mixture is stirred at 80°C for 60 minutes. In the resulting prepolymer mixture it is no longer possible to detect isocyanate groups by IR spectroscopy. A slightly turbid prepolymer 10 is obtained which at 20°C with a viscosity of 285 Pas can be poured and further-processed without problems.

Preparation of prepolymer blends (M):

General procedure (the specific amounts for the 15 individual components can be taken from Table 5. Where individual components are absent, the respective incorporation steps are omitted.):

Added to the prepolymer (A) described above is 20 carbamatomethyltrimethoxysilane (C-TMO, prepared according to Example 3) followed by mixing in a Speedmixer (DAC 150 FV from Hausschild) at 27 000 rpm for 15 seconds. Then chalk (BLR 3 from Omya), HDK V 15 (Wacker Chemie GmbH, Germany) and methoxymethyl- 25 trimethoxysilane (MeO-TMO, prepared according to Example 2) are added and the components are mixed twice for 20 seconds at a speed of 30 000 rpm. Finally aminopropyltrimethoxysilane (A-TMO Silquest® A1110 from Crompton) is added, followed again by mixing for 30 20 seconds at a speed of 30 000 rpm.

Table 5:

Batch number	C.Ex. 2-1	C.Ex. 2-2	C.Ex. 2-3
Polymer [%]	96%	65%	60%
Chalk BLR 3 [%]	-	30%	30%
HDK V-15 [%]	-	-	5%
Silane1 [%]	-	1% C-TMO	1% C-TMO
Silane2 [%]	2% MeO-TMO	2% MeO-TMO	2% MeO-TMO
Silane3 [%]	2% A-TMO	2% A-TMO	2% A-TMO

Example 7:**Properties of the cured prepolymer blends**

5 This example shows the properties and the production of the specimens of Example 6 and Comparative Example 2:

10 The finished prepolymer blends are coated out using a doctor blade into a Teflon® mold 2 mm high, the rate of curing through volume being approximately 2 mm in a day. After two-week storage, S1 test specimens are punched out, and their tensile properties are measured in accordance with EN ISO 527-2 on the Z010 from Zwick. The properties determined in this case for the respective prepolymer blends are listed in Table 7. The 15 blends of

- Example 5.1, Comparative Example 2.1
- Example 5.2, Comparative Example 2.2
- Example 5.3, Comparative Example 2.3

20 are in each case identical and differ only in the prepolymer used. In other words, the properties of these compositions can be compared directly with one another in each case.

Table 7:

Batch number	Ex. 5-1	Ex. 5-2	Ex. 5-3
Skinning time	> 2 h	> 2 h	18 min
Tensile strength [MPa]	0.49	1.29	3.81
Breaking elongation [%]	278.01	418.13	606.78
Modulus [MPa]	0.25	0.5	1.3
Shore hardness	20	31	46
Batch number	C.Ex. 2-1	C.Ex. 2-2	C.Ex. 2-3
Skinning time	> 1.5 h	> 1.5 h	2 min
Tensile strength [MPa]	0.47	1.08	2.58
Breaking elongation [%]	291.95	473.14	512.31
Modulus [MPa]	0.18	0.34	0.85
Shore hardness	15	20	38